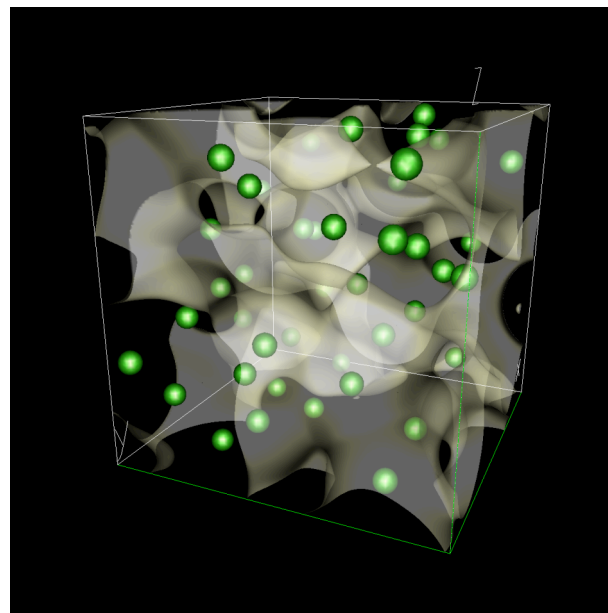
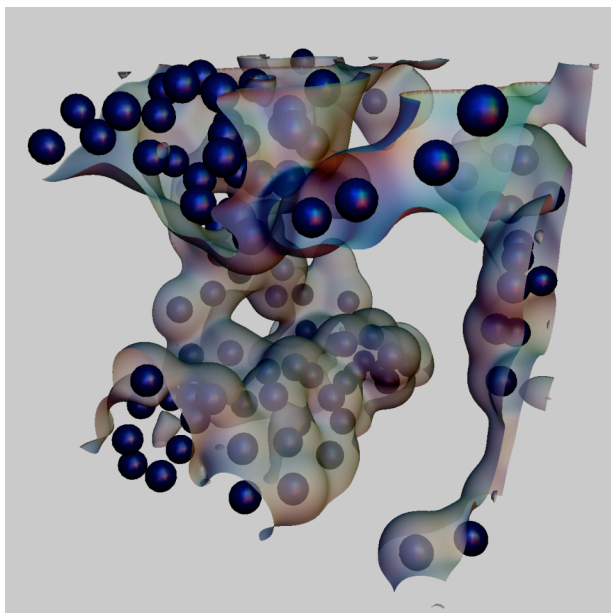


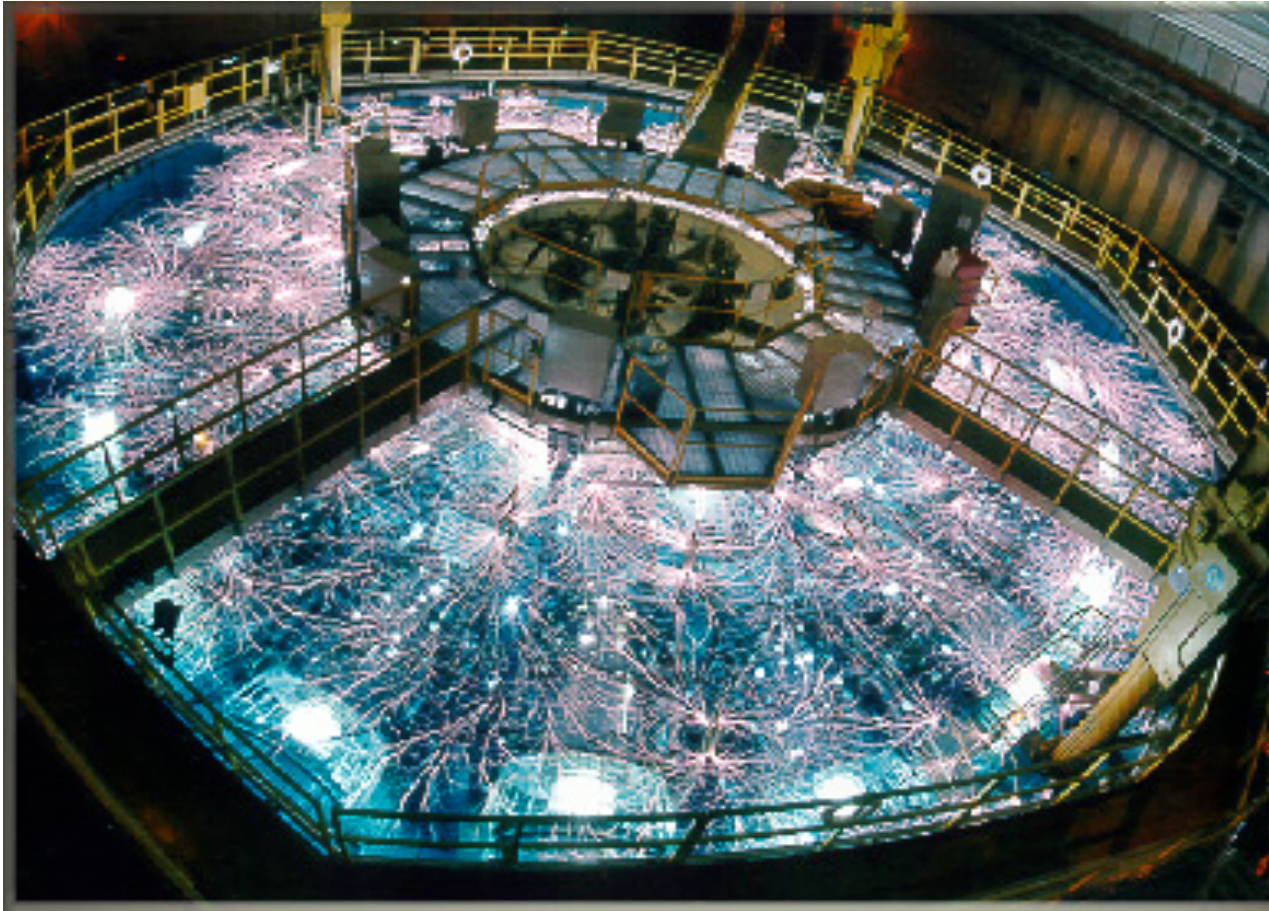
Quantum Molecular Dynamics Calculations of Warm Dense Matter and Application to Pulsed Power Experiments



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Sandia National Laboratories

Warm Dense Matter Winter School
Lawrence Berkeley National Laboratory
January 10-16, 2008

At Sandia's Pulsed Power Sciences Center, much of what we do is considered High Energy Density Physics (HEDP)



Z pinches for Inertial Confinement Fusion

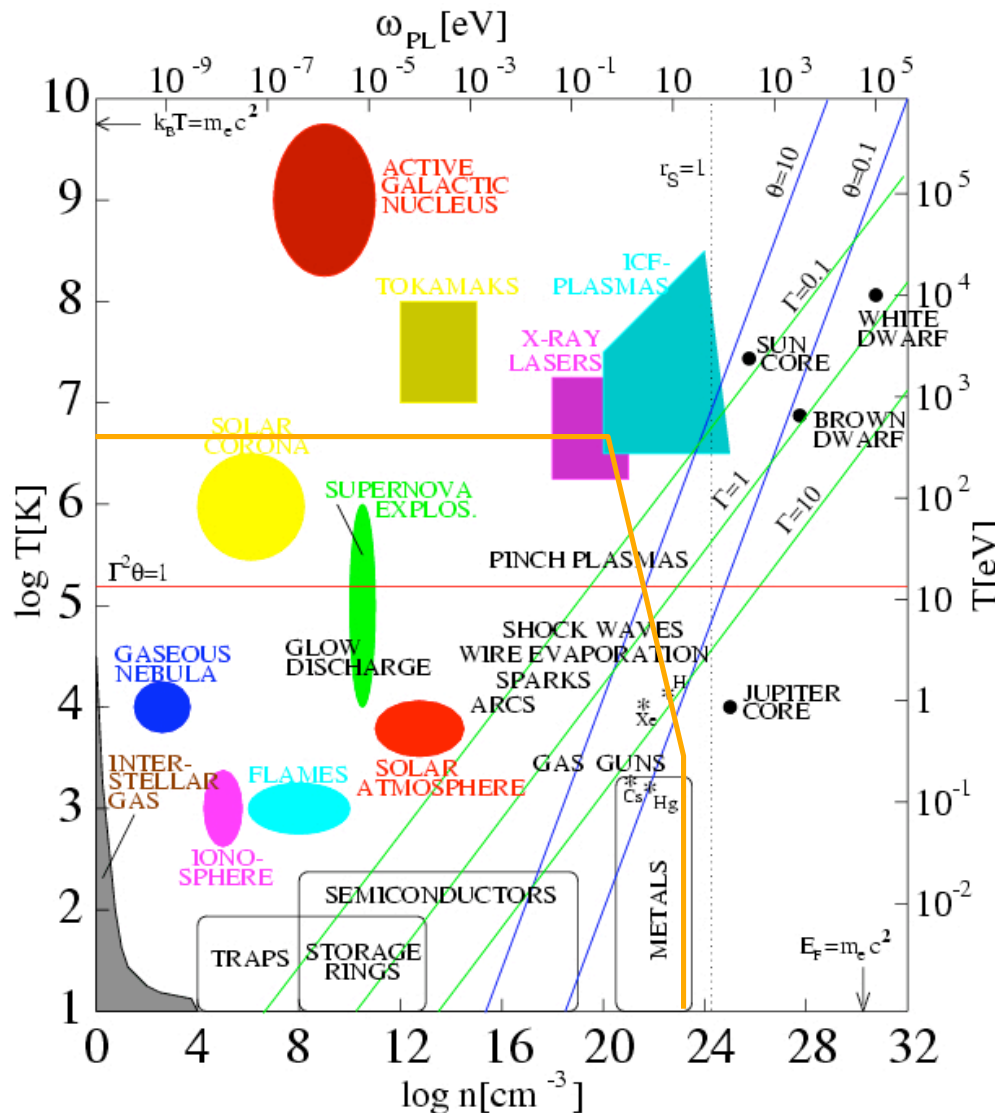
Magnetically launched flyer plates for EOS studies

Isentropic compression for EOS studies

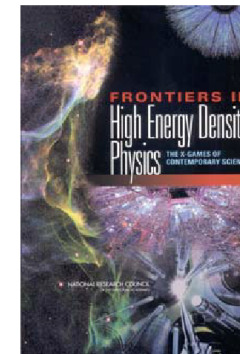
Studies of material melt boundaries: shock melting of Be and diamond

The Z machine delivers more than 25 million Amperes of current

A recent National Academy of Sciences Committee* has defined High Energy Density as $> 10^{11} \text{ J/m}^3$ or Total Pressures $> 1 \text{ Mbar}$

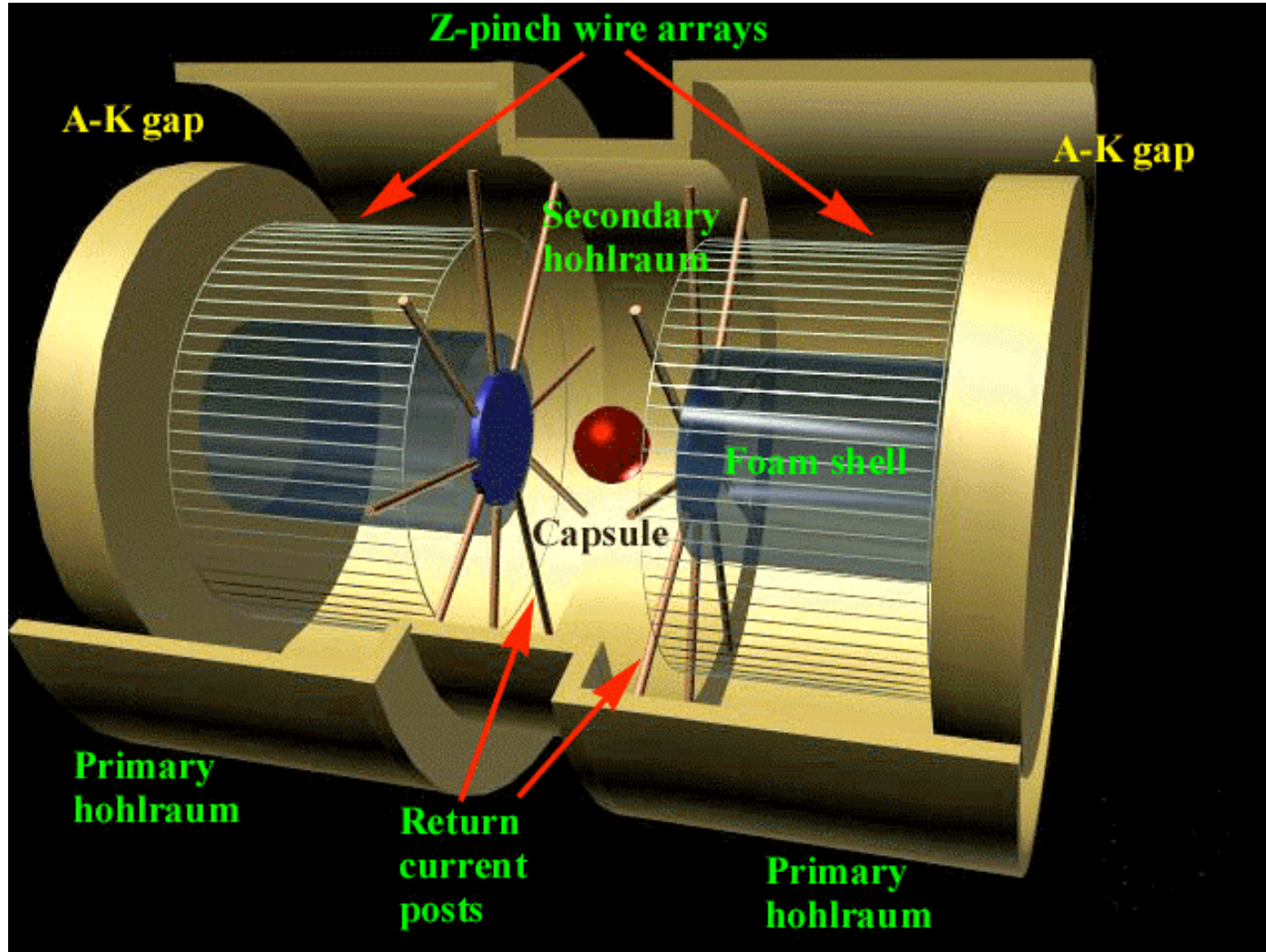


The HEDP region is above and to the right of the orange line



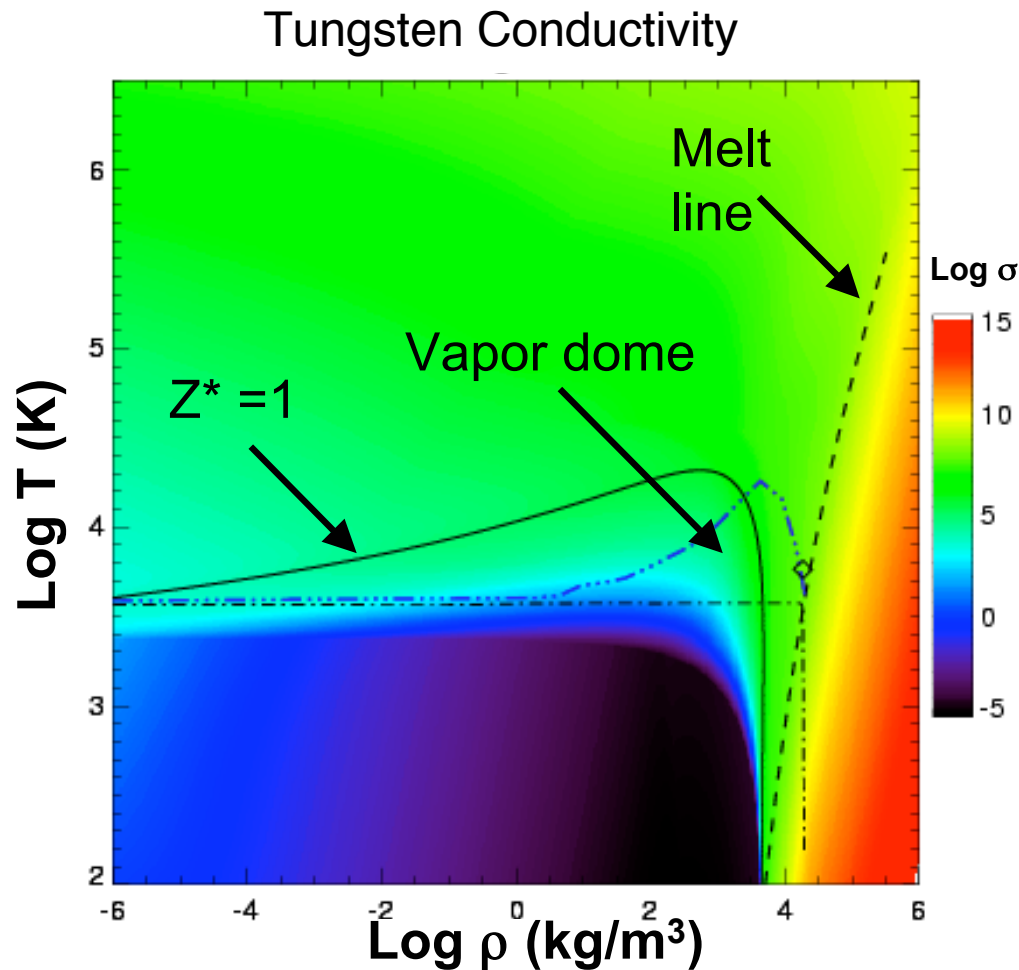
*Chaired by Ron Davidson, see their report: "Frontiers in High Energy Density Physics: The X-Games of Contemporary Science", National Academy Press

We routinely perform large scale computer simulations to model the complex geometries and physics in our HEDP experiments



This is a double-ended Z pinch with an ICF target in the center

HEDP computer simulations rely on “physics packages”: Conductivities, Equations of State, and Opacities



Degeneracy and magnetization effects

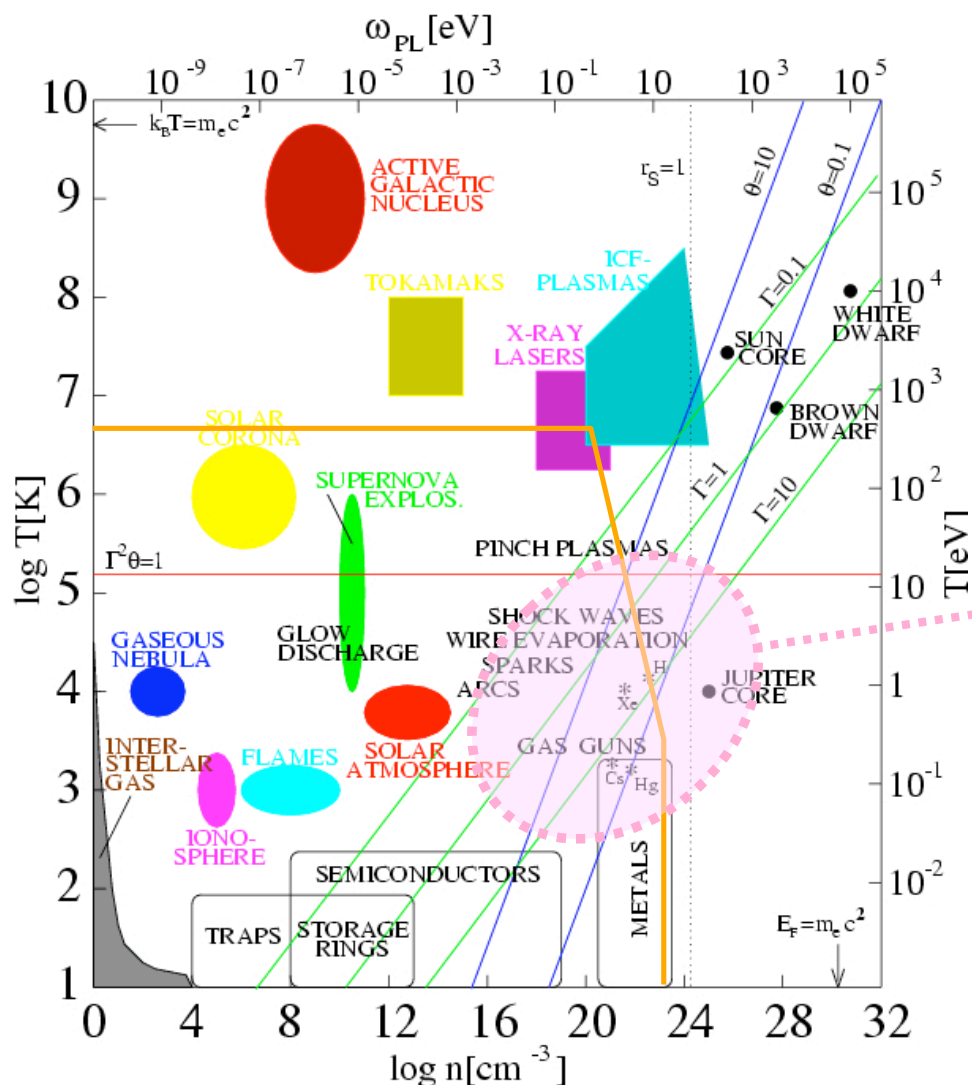
$$\sigma = n_e A\left(\frac{\mu}{kT}, \Omega\tau\right) \frac{e^2}{m} \tau$$

Pressure ionization, metal-insulator transition, Thomas-Fermi at high T, ρ

Coulomb and electron-neutral collisions, Bloch-Gruneisen solid, Lindemann melting law

This highly structured portion of phase space is Warm Dense Matter

The “Warm Dense Matter” region of phase space is the most problematic for developing accurate physics models

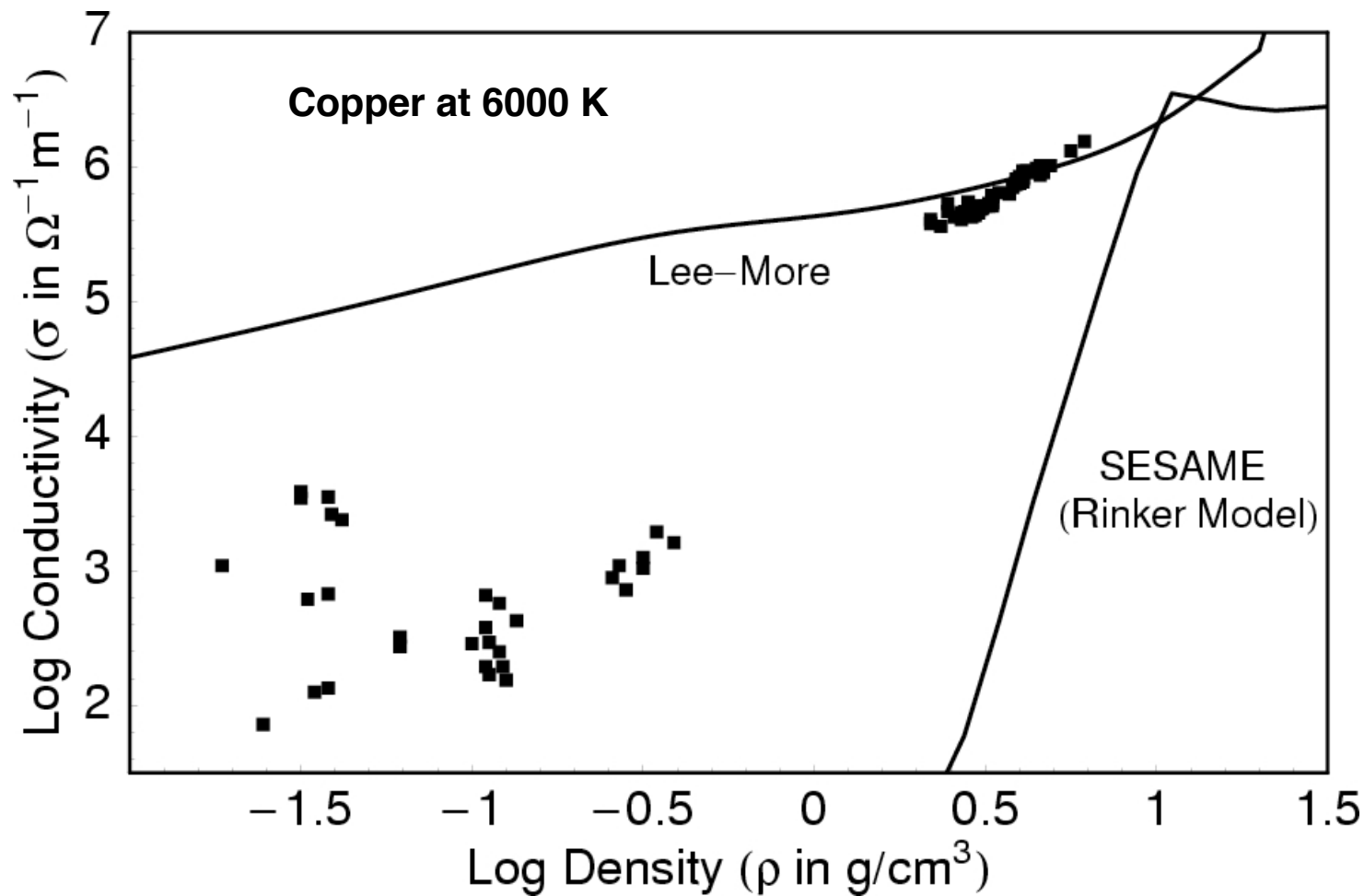


Definitions of Warm Dense Matter are varied, but generally center around **strongly coupled ions and moderately degenerate electrons** --- many different interactions are comparable.

A **quantum mechanical** treatment is generally necessary.

Most wide-range equations of state interpolate through this difficult area.

The Lee-More and SESAME (Rinker) conductivity models are inaccurate near the metal-insulator transition

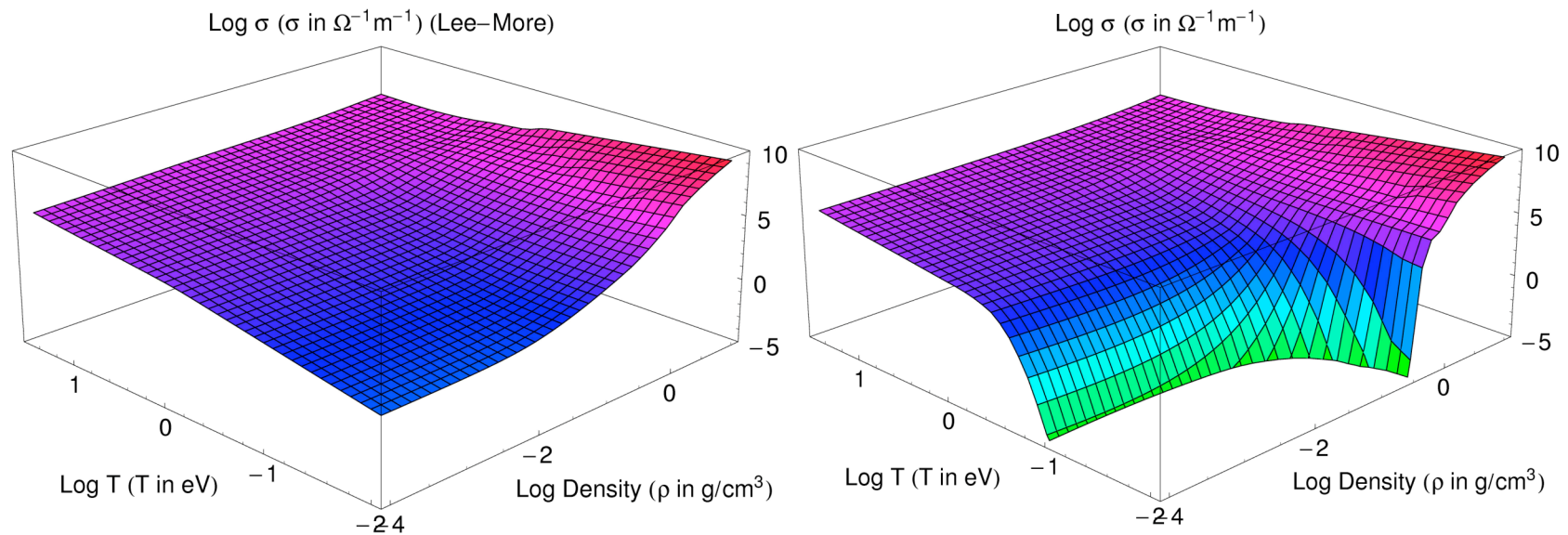


Data courtesy of Alan DeSilva, University of Maryland

Modifications of the Lee-More algorithm were made to obtain an improved wide-range model*



* M. P. Desjarlais, Contrib. Plasma Phys. **41** (2001) 2-3, 267-270



Principal modifications:

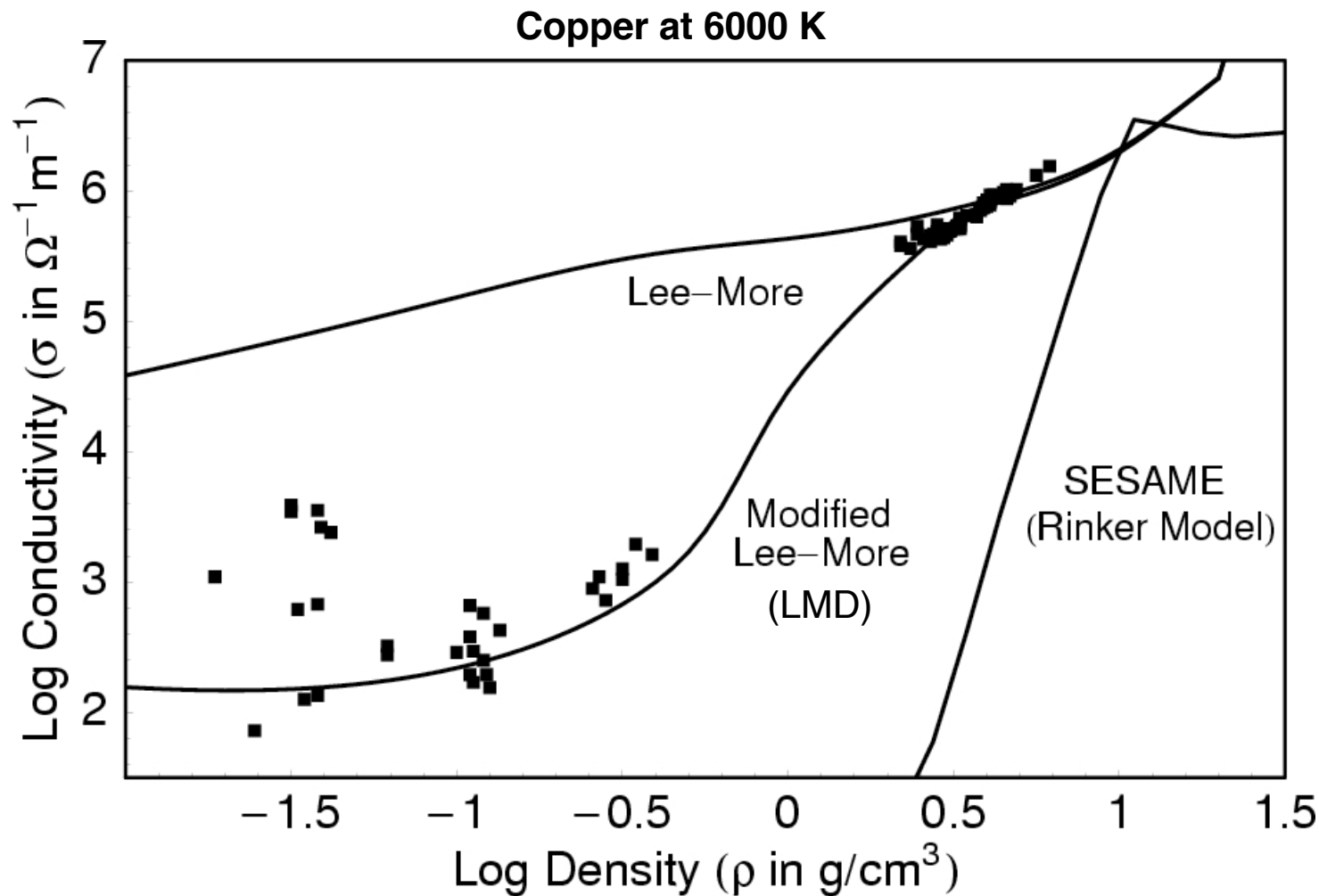
$$\sigma = n_e A\left(\frac{\mu}{kT}, \omega\tau\right) \frac{e^2}{m} \tau$$

Ionization equilibrium model, pressure ionization

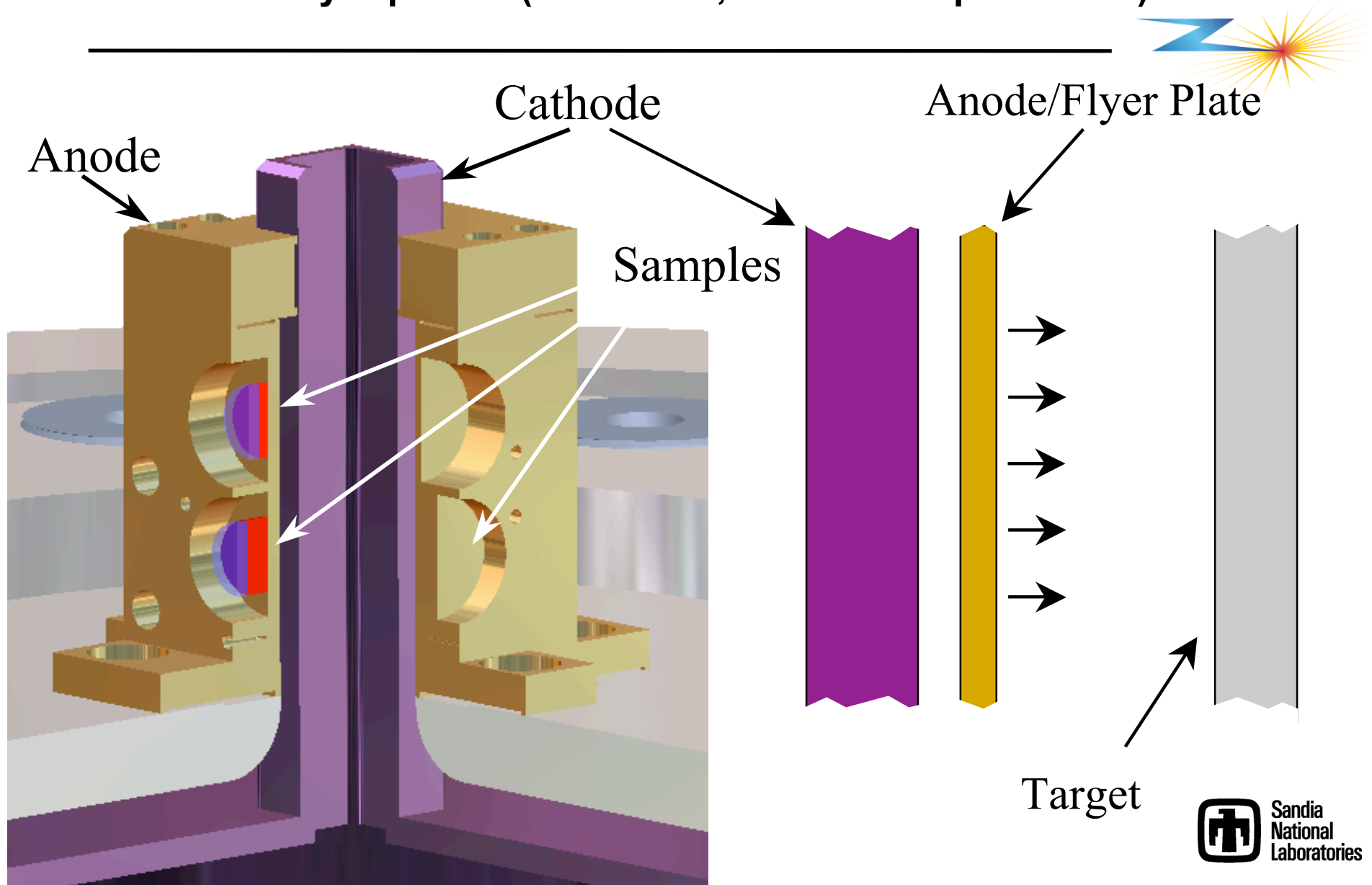
Electron-neutral collisions,
Minimum collision time



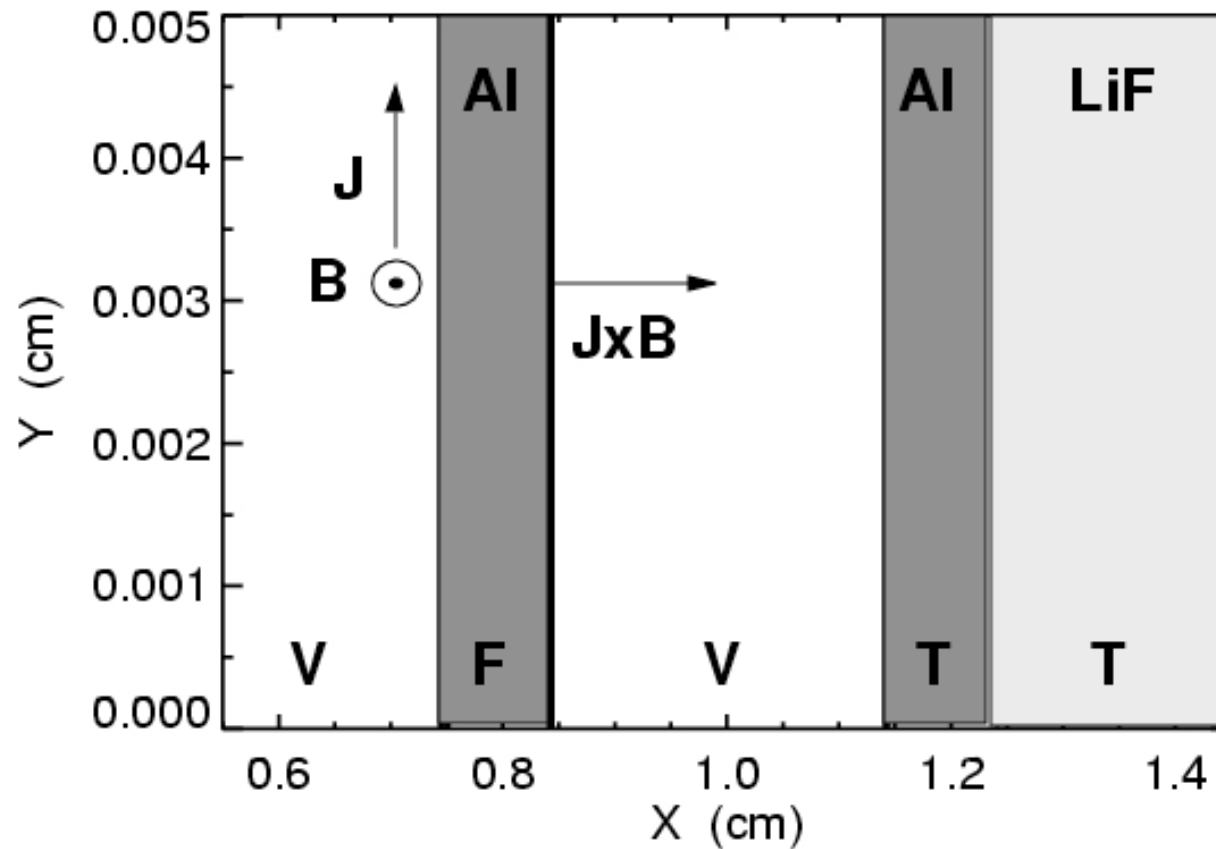
This modified Lee-More model provides much better agreement with DeSilva's copper data



A demanding application: Ultra-high velocity magnetically launched flyer plates (30 km/sec, Multi-Mbar pressures)



Simulation geometry for a magnetically launched flyer plate

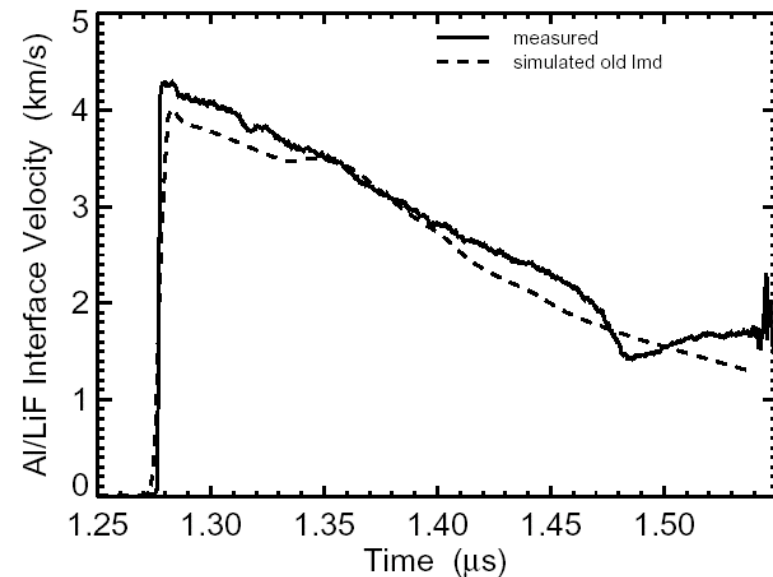
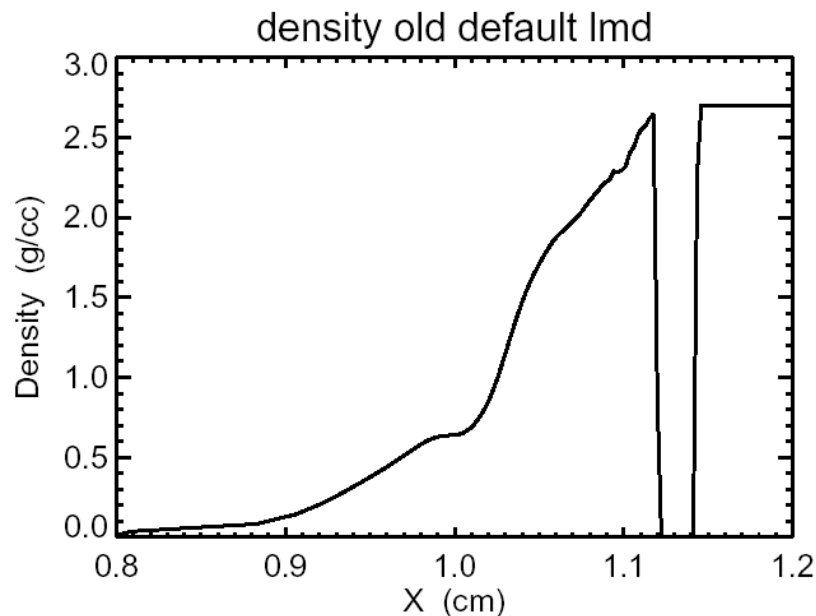


We simulated these magnetically launched flyer plates using the modified Lee-More (LMD) conductivities



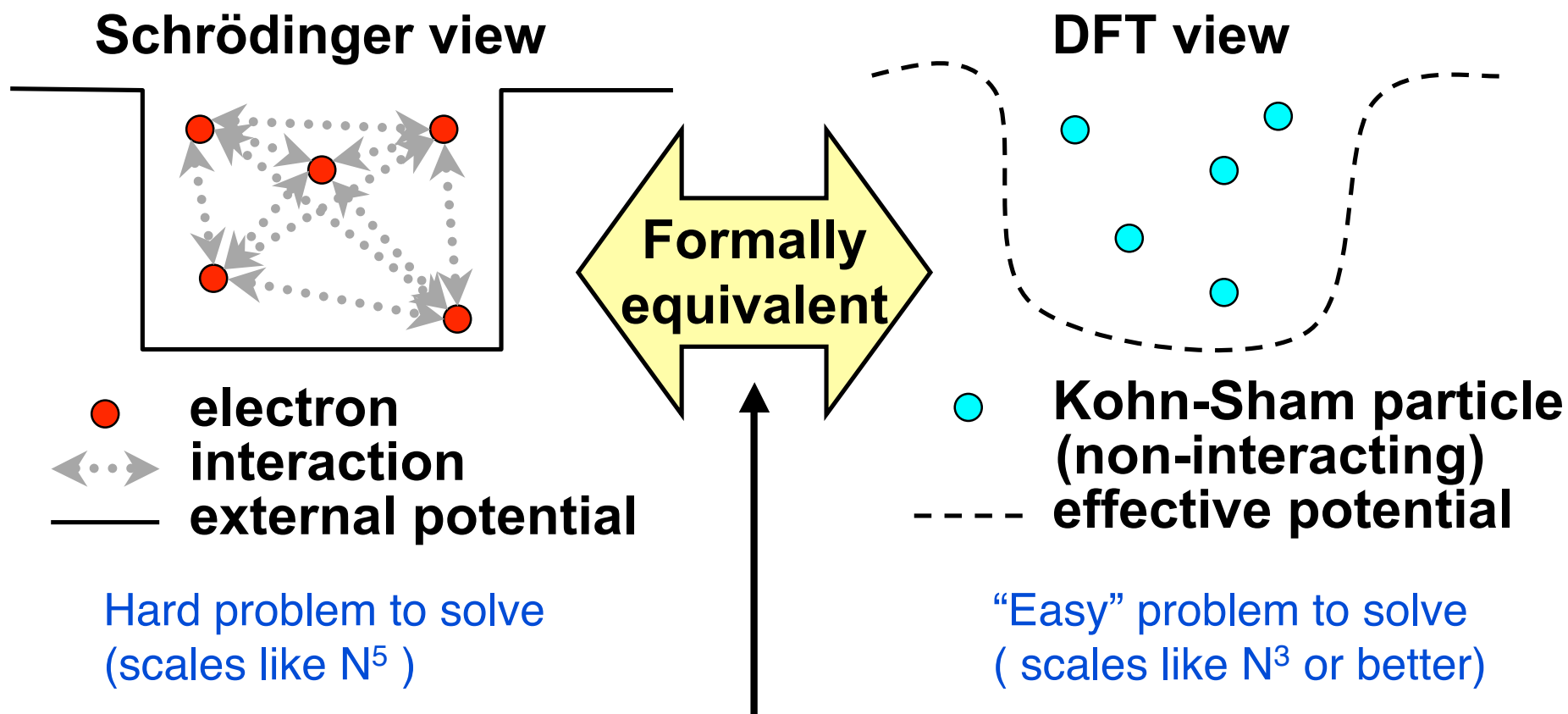
Detailed comparison between simulations and experiments for magnetically launched flyer plates suggested that our *improved* conductivities were still not sufficiently accurate for the warm dense liquid aluminum.

Simulations by Ray Lemke with Sandia's 3D Rad-MHD ALEGRA code



For many of our applications we require conductivities accurate to well within a factor of two.

Density Functional Theory (DFT) is a formally exact representation of the N electron Schrödinger Equation



Hohenberg and Kohn proved this (1964)

Nobel prize in Chemistry for Kohn in 1998

We are using Density Functional Theory (DFT) to perform Quantum Molecular Dynamics (QMD) simulations of Warm Dense Matter



Density Functional Theory is formally exact, but is, in practice, a good approximate solution to the N electron Schrödinger equations. DFT is a work-horse tool in condensed matter physics, but a relative newcomer to Warm Dense Matter and High Energy Density Physics.

QMD: The **Kohn-Sham*** **DFT** equations are solved for a given atomic configuration (fixed in the Born-Oppenheimer approximation) and the **quantum mechanical forces** on all the atoms are calculated from the wavefunctions following the Feynman-Hellmann theorem, **the atomic positions are advanced classically**, and a new solution to the DFT equations is calculated.

*Kohn and Sham, 1965

See Car and Parrinello (PRL, 1985), for the original DFT/QMD paper.

What do the Kohn-Sham equations look like?



$$\left(-\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}_1) \right) \Psi_i = \varepsilon_i \Psi_i$$

Electron and Ion Coulomb terms

$$V_{eff}(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 - \sum_A \frac{Z_A}{r_{1A}} + V_{xc}(\vec{r}_1)$$

Exchange and Correlation

We don't know this piece exactly, but simple approximations work surprisingly well

$$V_{xc}(\vec{r}_1) \equiv \frac{\delta E_{xc}[\rho(\vec{r}_1)]}{\delta \rho(\vec{r}_1)} \quad \text{where } E_{xc} \text{ is the Exchange and Correlation Functional,}$$

e.g., Dirac exchange ($C_x \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1$), LDA, GGA, Exact Exchange,

$$\rho(\vec{r}_1) = \sum_i f_i |\Psi_i(\vec{r}_1)|^2 \quad (\text{The } f_i \text{ are Fermi occupation numbers})$$

Details of the QMD simulations



- The simulations are performed with VASP (Vienna Ab initio Simulation Program), a plane wave density functional code.
- Exchange and Correlation functionals are typically Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA).
- We typically use up to 250 atoms, but it varies depending on density and the number of electrons we need to carry (the valence) ; We use Projector Augmented Wave (PAW) all-electron, frozen core potentials for the atoms.
- We generally perform our simulations in the Canonical Ensemble (N,V,T) using either velocity scaling or a Nosé-Hoover thermostat to regulate the temperature; Fermi statistics for the electrons.
- Typical runs cover one to tens of picoseconds.

Frequency-dependent electrical conductivities are calculated with the Kubo-Greenwood formula



$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_{\alpha=1}^3 \sum_{j=1}^N \sum_{i=1}^N (F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}})) \left| \langle \Psi_{j,\mathbf{k}} | \nabla_{\alpha} | \Psi_{i,\mathbf{k}} \rangle \right|^2 \delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega),$$

where e and m are the electron charge and mass. The i and j summations are over the N discrete bands of the triply periodic calculation for the cubic supercell with volume Ω . The coordinate index is α and in general we average over α to improve the statistics. $F(\varepsilon_{i,\mathbf{k}})$ is the Fermi weight corresponding to the energy for the i -th band at \mathbf{k} with wavefunction $\Psi_{i,\mathbf{k}}$.

We integrate over the Brillouin zone using the method of special \mathbf{k} -points

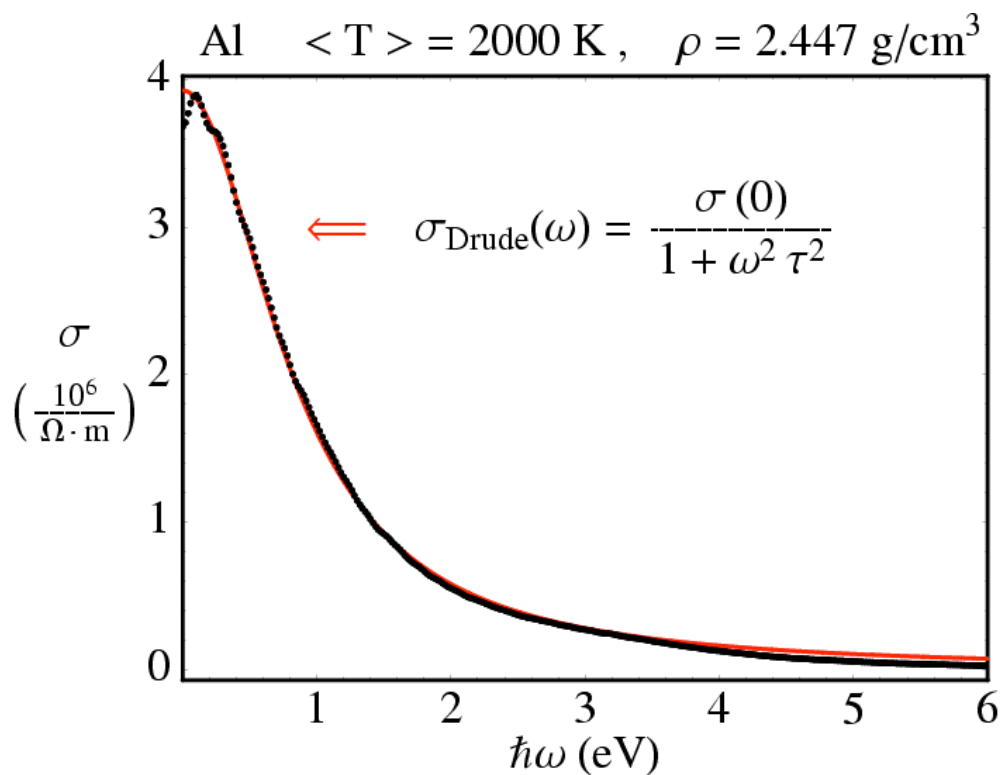
$$\sigma(\omega) = \sum_{\mathbf{k}} \sigma_{\mathbf{k}}(\omega) W(\mathbf{k}) ,$$

and average over 10 to 20 configurations selected from the MD run.

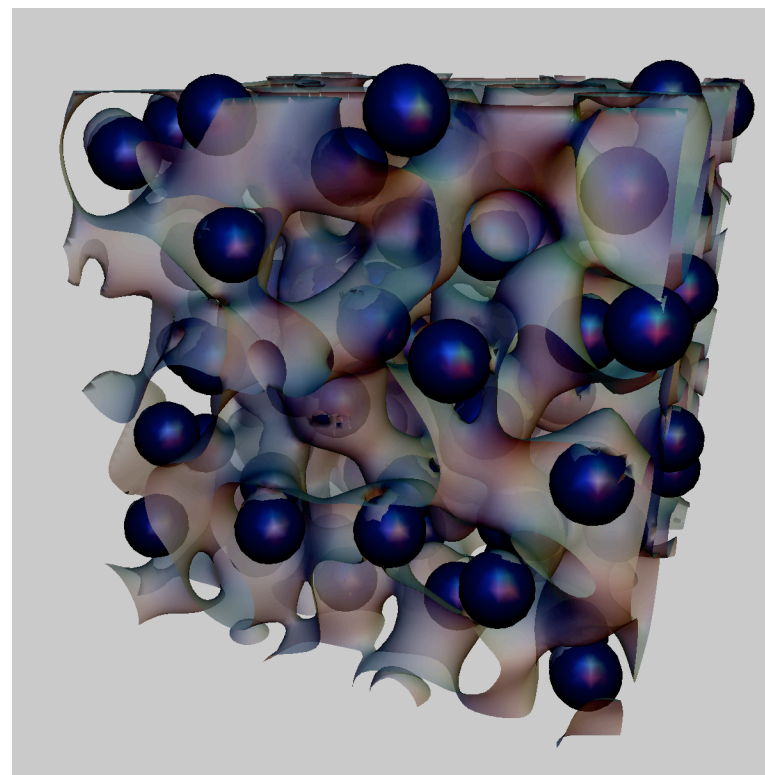
This representation of the conductivity is really nothing more than the quantum analog of the classical current-current correlation function.

Includes electron-ion, electron-neutral, and electron-electron contributions

At liquid aluminum densities just below solid, the optical conductivity is well fit by the Drude model

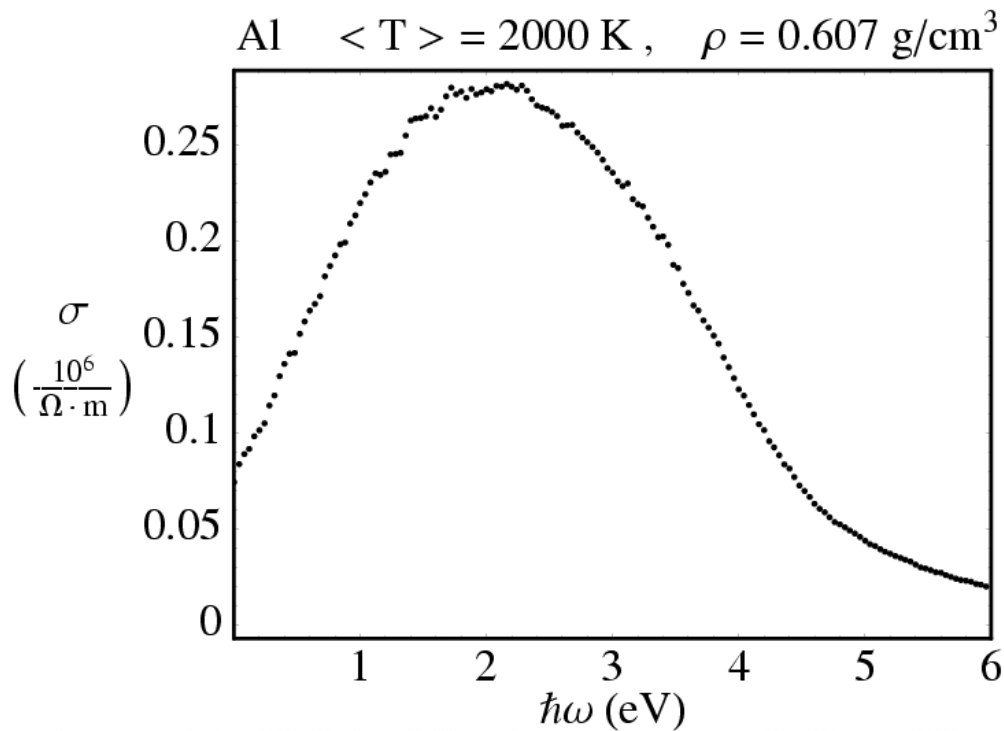


The agreement with the Drude model indicates 'nearly free' electrons

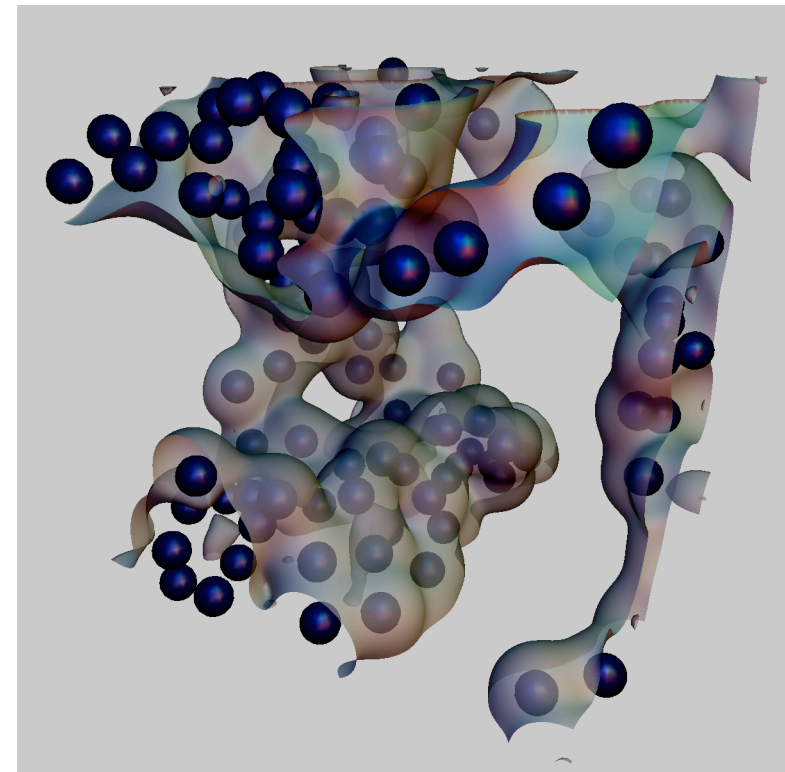


Ion cores displayed with iso-surfaces of the mean valence charge density

At lower density, where phase separation is pronounced, a gap begins to form at low energy



The dc conductivity has dropped by a factor of 25 for a factor of 4 drop in density

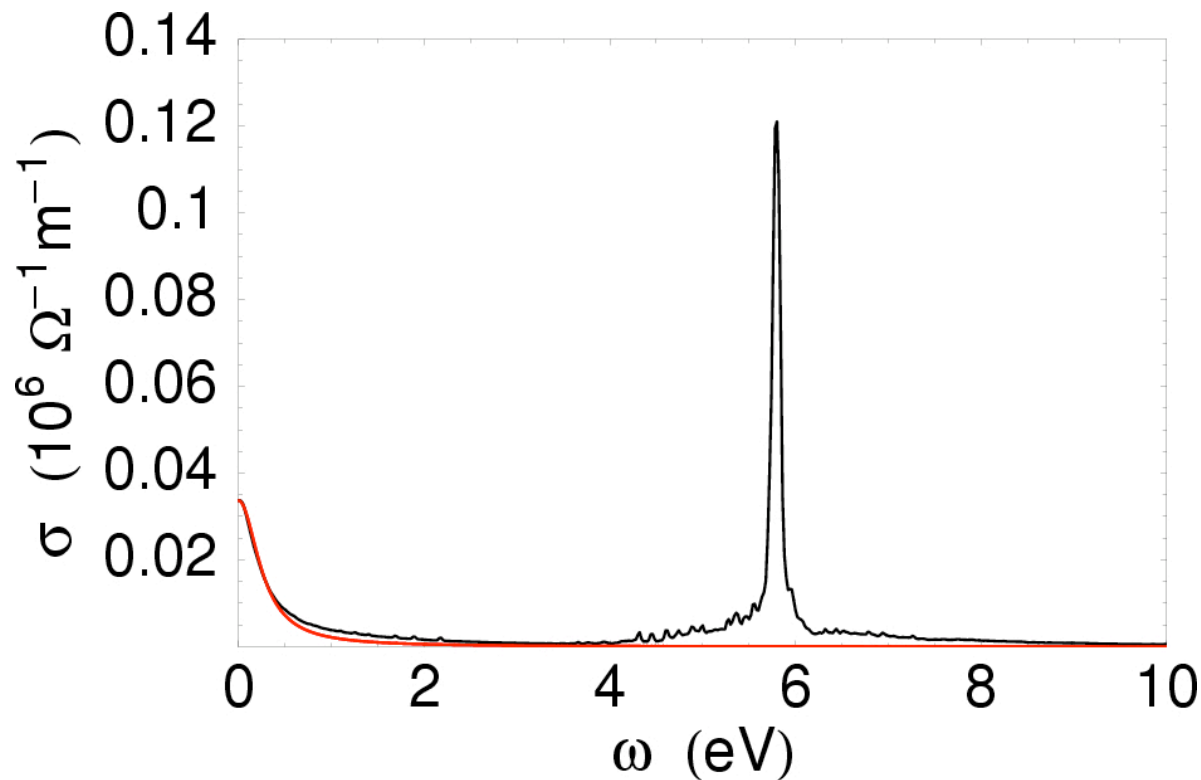


Note the pronounced separation into liquid and void (vapor) regions

At low densities and higher temperatures, a Drude component re-emerges in the optical conductivity



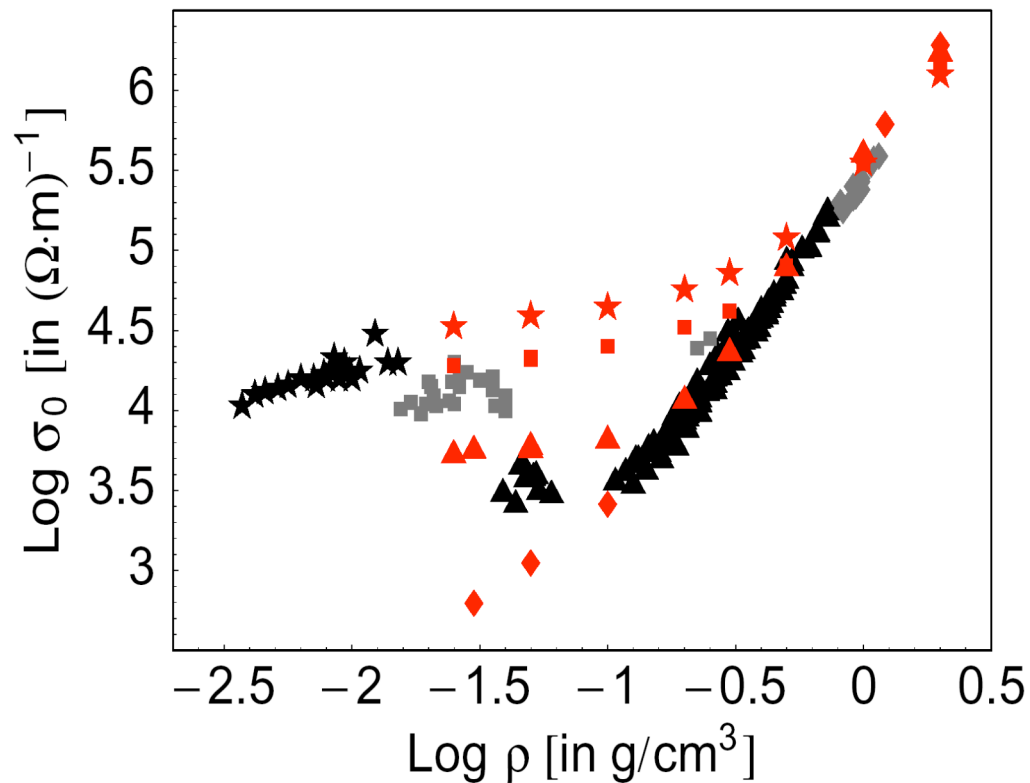
The optical conductivity for 0.025 g/cc at 30000 K



We have gone from condensed matter to an ideal plasma!

The peak at about 5.8 eV is characteristic of a 3s->3p transition of the isolated ion.

The QMD-KG results are in good agreement with DeSilva's data over a two decade range of density

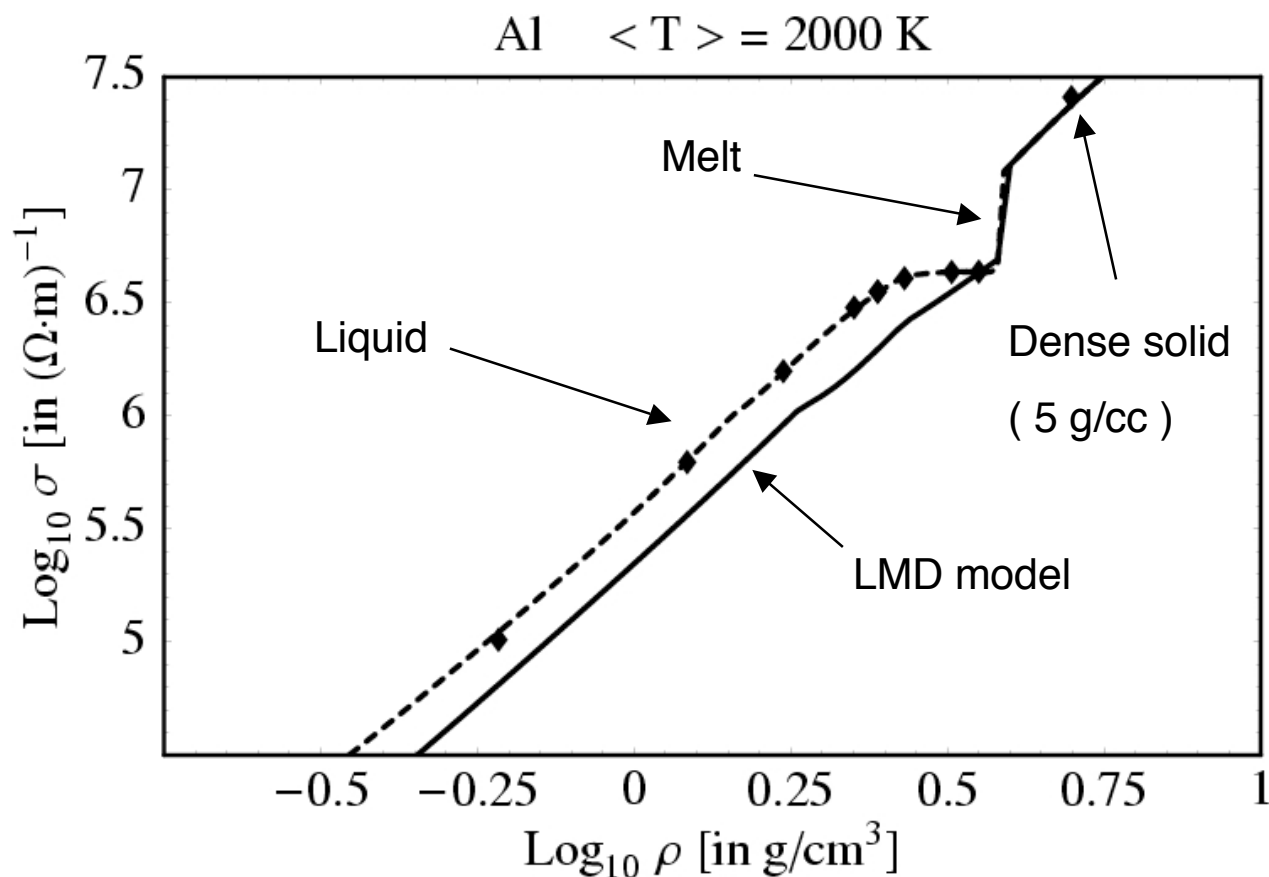


DeSilva and Katsouras data in black or grey, QMD-KG results in red

★ 30000 K, ■ 20000 K, ▲ 10000 K, ◆ 6000 K

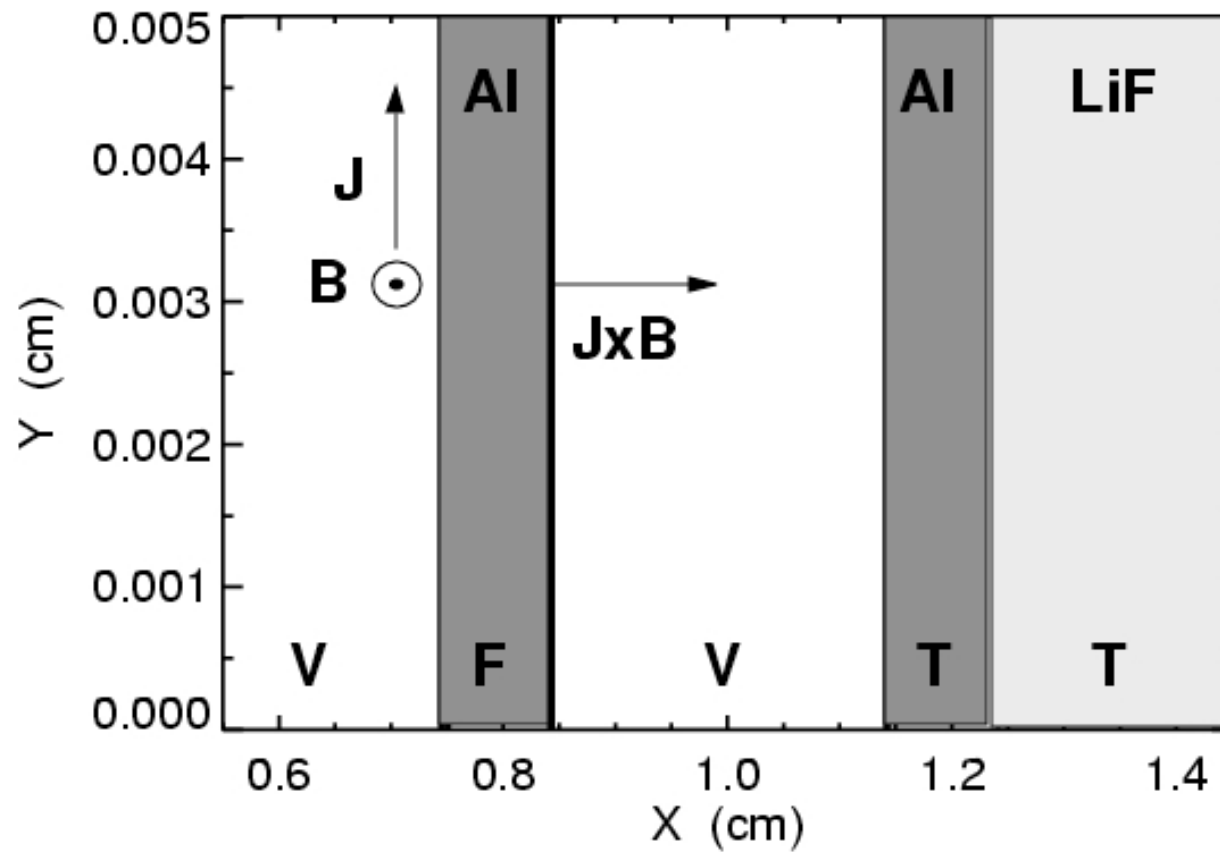
[Desjarlais, Kress, and Collins, Phys. Rev. E **66**, 025401 (2002)]

The calculated liquid aluminum conductivities are higher than the *modified* Lee-More (LMD) model predictions



The dashed line shows the 2000 K isotherm from our QMD-tuned wide-range aluminum model

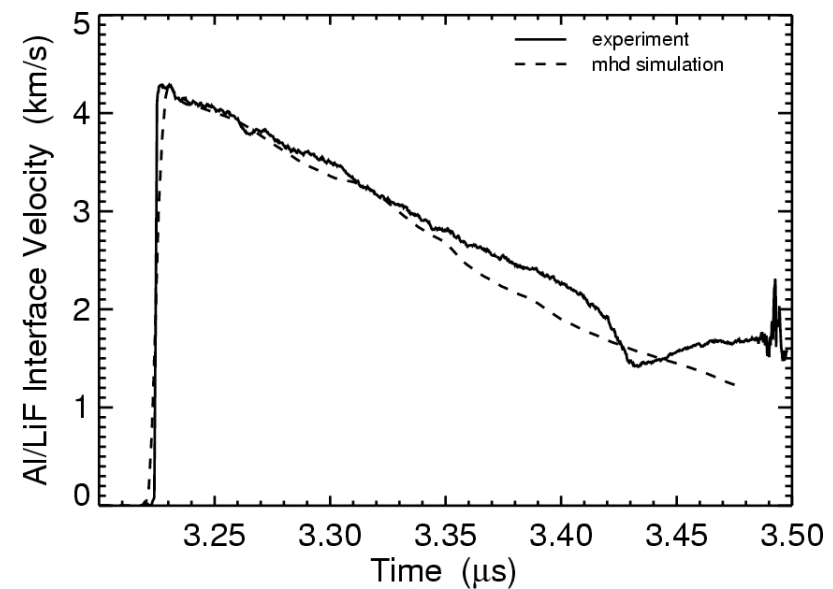
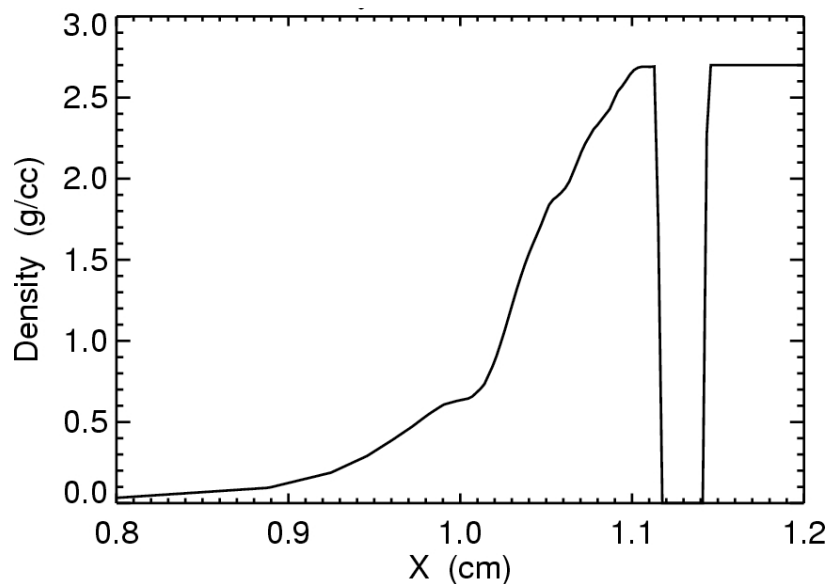
The magnetically launched flyer plate geometry



Flyer plate simulations with the QMD based conductivities give very good agreement with experiment

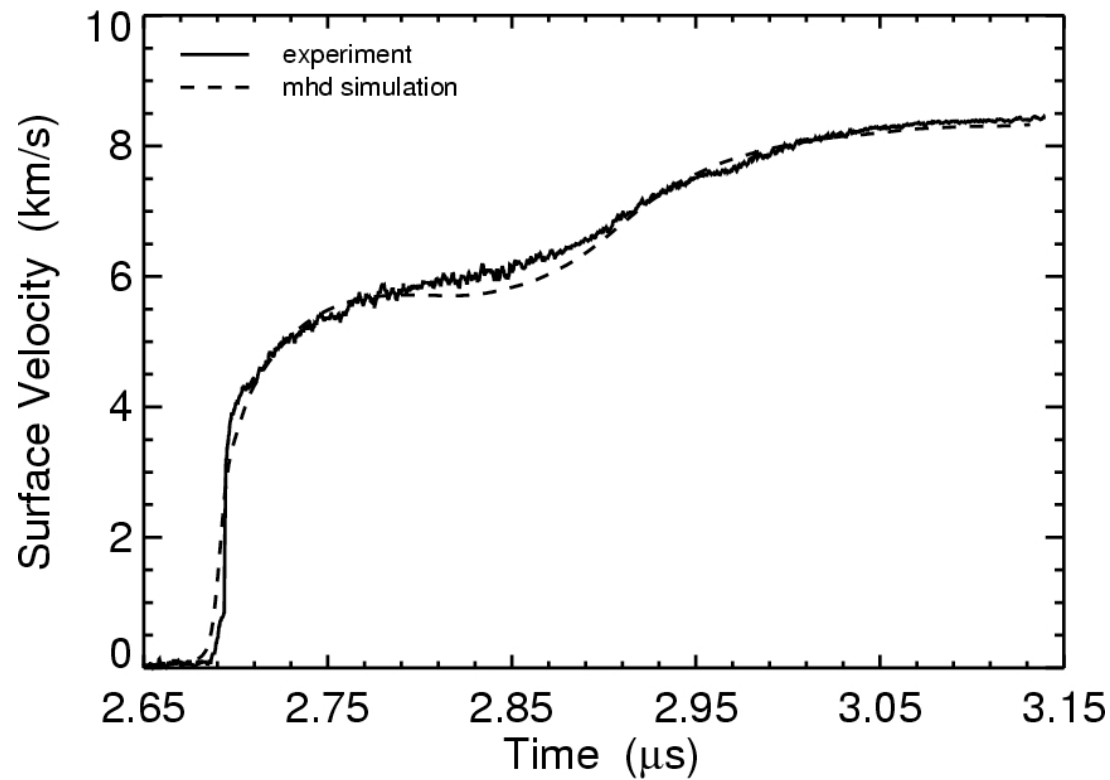


Simulations by Ray Lemke with Sandia's 3D Rad-MHD ALEGRA code

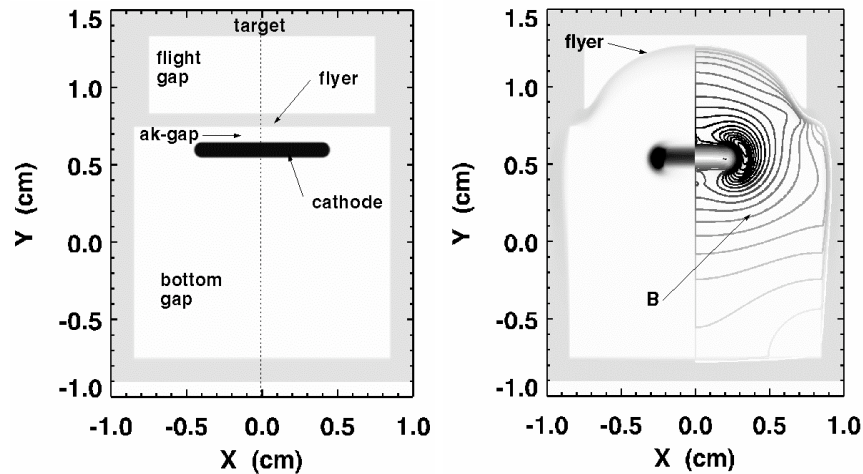


Conductivities based on the QMD calculations have given us a new predictive capability.

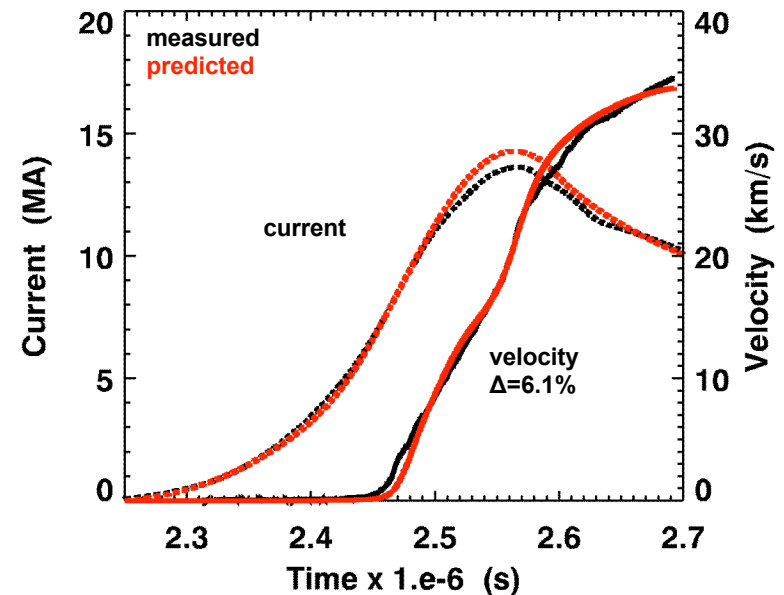
**Simulations of the flyer velocities with ALEGRA
(our Rad-Hydro code) are now in very good agreement with
experiments**



We have used our simulation capability with the new aluminum model to optimize flyer performance on Z



Measured / predicted current & flyer velocity (850 μm Al)



The simulations were performed by Ray Lemke using Sandia's ALEGRA code in 2-D

In recent years there has been renewed interest in the liquid deuterium Hugoniot



The Hugoniot is the locus of single shock end states satisfying the Rankine-Hugoniot conditions for various U_s

Mass
conservation

$$\rho_1 / \rho_0 = U_s / (U_s - u_p)$$

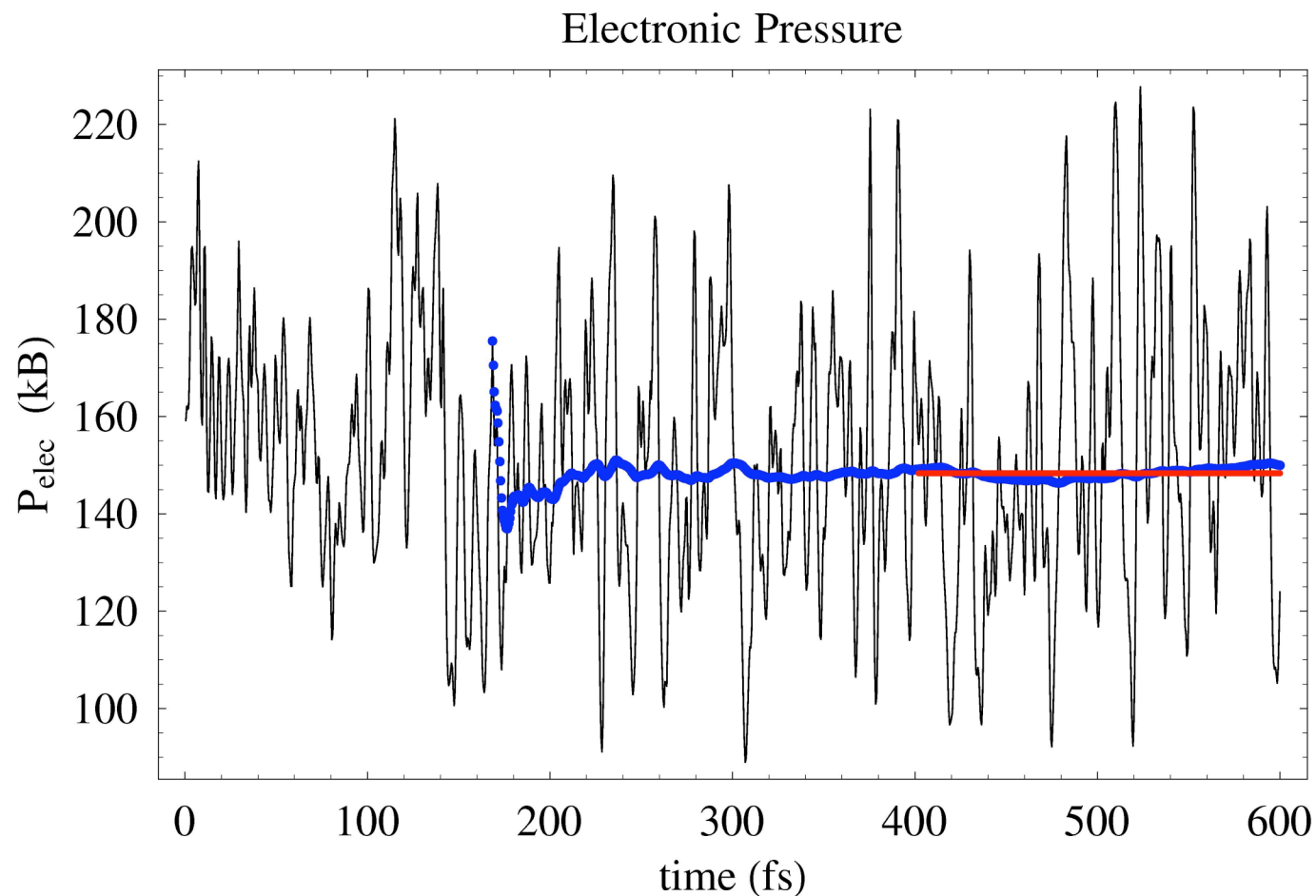
Momentum
conservation

$$U_s u_p = (P_1 - P_0) / \rho_0$$

Energy
conservation

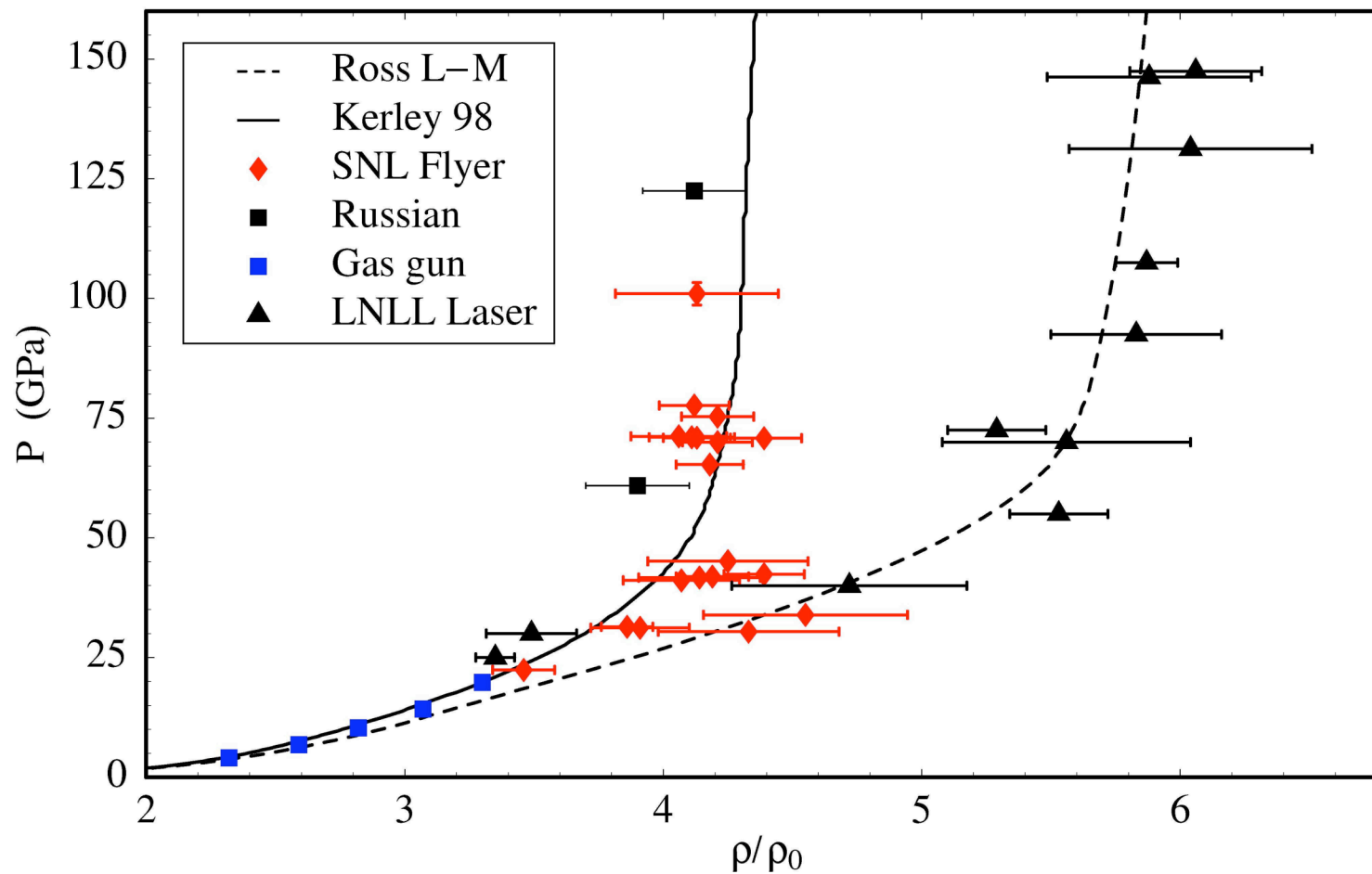
$$E_1 - E_0 = \frac{P_1 + P_0}{2} (V_0 - V_1)$$

Thermodynamic averages are taken as local averages of a cumulative average



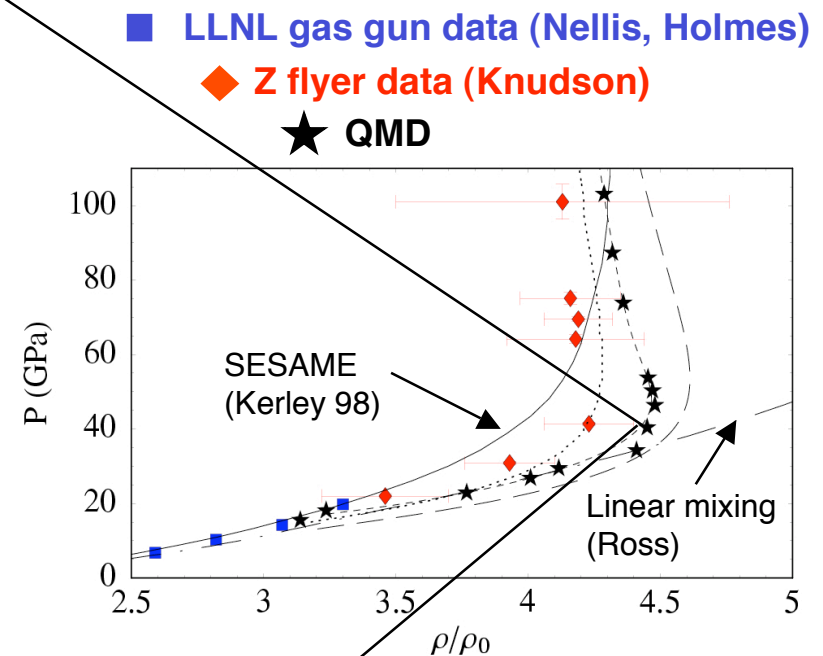
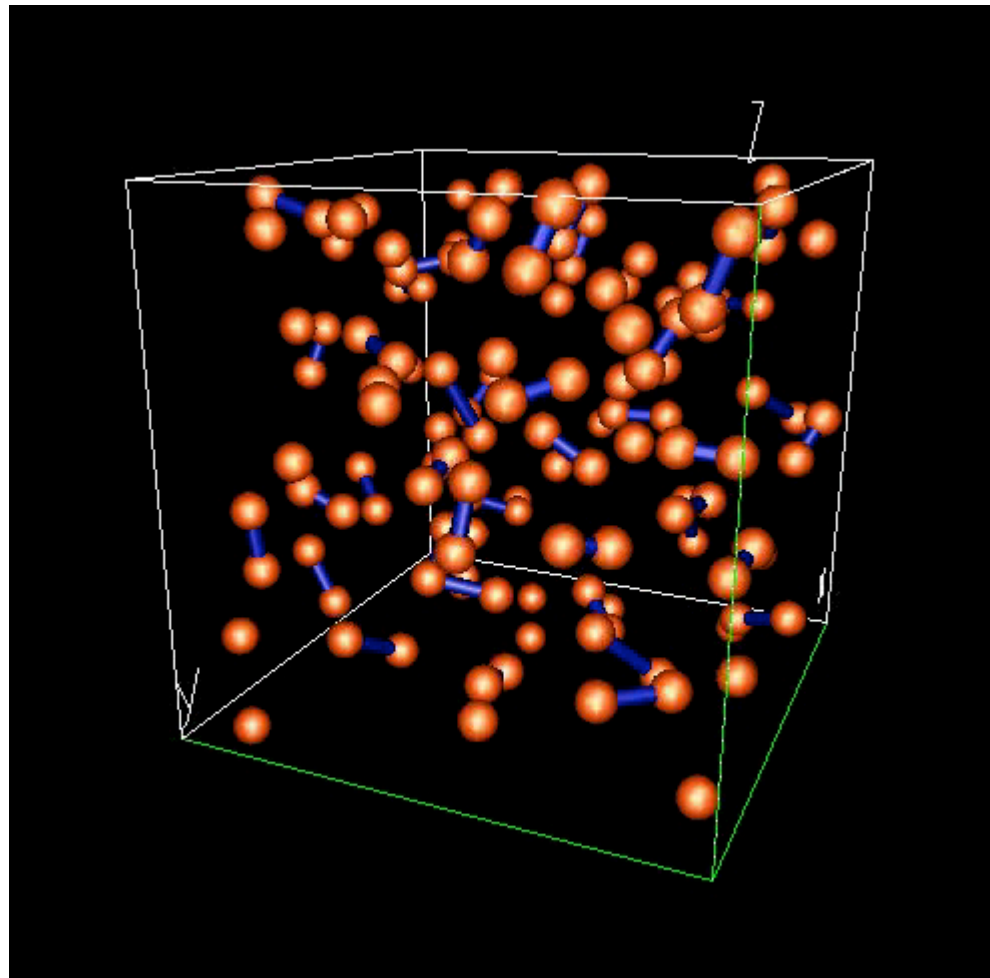
We make heavy use of VASP specific Mathematica notebooks to analyze the QMD runs and build EOS and conductivity databases

The Livermore laser driven shock data suggested a considerably softer D_2 Hugoniot than the Sandia data



D_2 Hugoniot data from Z courtesy of Marcus Knudson

We have used quantum molecular dynamics to study the principal Hugoniot of shocked liquid deuterium



Our QMD simulations of D_2 indicate a Hugoniot in very good agreement with data from Sandia's Z machine

Other optical properties are obtained through the Kramers-Krönig relations for $\sigma(\omega)$



Through the Kramers-Kronig relations we have $\sigma_2(\omega) = -\frac{2}{\pi} P \int \frac{\sigma_1(\omega')}{\omega'^2 - \omega^2} d\omega'$

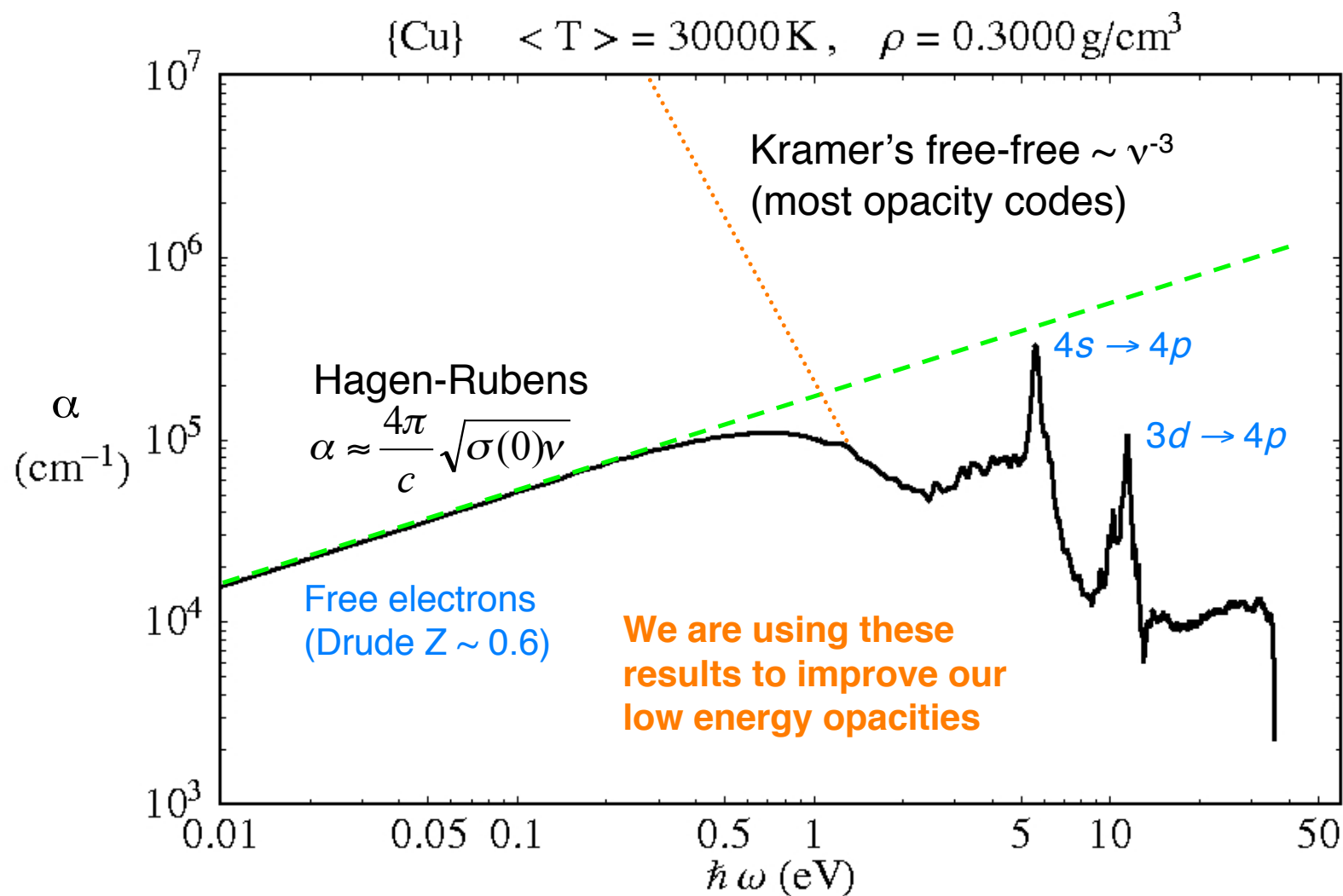
where P indicates the principal value of the integral. The dielectric function is then given by $\epsilon_1(\omega) = 1 - \frac{4\pi}{\omega} \sigma_2(\omega)$ and $\epsilon_2(\omega) = \frac{4\pi}{\omega} \sigma_1(\omega)$

Defining $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \equiv [n(\omega) + ik(\omega)]^2$ we can write the reflectivity $r(\omega)$ and absorption coefficient $\alpha(\omega)$:

$$r(\omega) = \frac{[1 - n(\omega)]^2 + k(\omega)^2}{[1 + n(\omega)]^2 + k(\omega)^2}, \quad \alpha(\omega) = \frac{4\pi}{n(\omega)c} \sigma_1(\omega).$$

We can now improve our low energy (below ~ 30 eV) opacities $\alpha(\omega)/\rho$ where ρ is the mass density.

The absorption has the proper Hagen-Rubens low frequency behavior, consistent with the dc conductivity



Some Cautions and Limitations of DFT and DFT/QMD



- DFT is a ground state theory (A thermal ground state – Fermi distribution for electrons – is okay; see Mermin, 1965)
- Eigenvalues and Wavefunctions are not “real”; they correspond to the non-interacting electrons. Why use them at all? Actually, wavefunctions not bad in most cases (verified with quantum Monte Carlo results).
- Band gaps are too small for insulators and semi-conductors (including expanded metals). Caused in part by the self-interaction error: electrons see their own potential to some degree through ρ and seek less localized orbitals. Leads to enhanced ionization and polarizabilities. (Get's better with higher temperature.) Non-local functionals (Exact Exchange, computationally expensive) can mitigate this problem.
- Ion motion is classical. Zero-point energy and zero-point pressure contributions are absent. Must be careful here, but corrections can usually be made.
- Which functional to use? LDA? GGA (PBE, PW-91, etc)? Exact Exchange? GGA generally favored for atoms, molecules, lighter element solids; LDA for heavier element solids. New functional developed at Sandia (AM05) appears to model both lighter and heavier element solids well (tested with lattice constants).

Background and Some Useful References



- Hohenberg and Kohn, *Inhomogeneous electron gas*, Phys. Rev. **136** B864 (1964).
- Kohn and Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. **140** A1133.
- Mermin, *Thermal properties of the inhomogeneous electron gas*, Phys. Rev. **137** A1441 (1965).
- Parr and Yang, *Density Functional Theory of Atoms and Molecules* (New York: Oxford University Press 1989)
- Car and Parinello, *Unified approach for molecular dynamics and density functional theory*, Phys. Rev. Lett. **55**, 2471 (1985).
- Payne, Teter, Allen, Arias and Joannopoulos, *Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients*, Rev. Mod. Phys. **64** 3865 (1992).

A DFT tutorial (with lots of references):

- Mattsson, Schultz, Desjarlais, Mattsson, and Leung, *Designing meaningful density functional theory calculations in materials science—a primer*, Modelling Simul. Mater. Sci. Eng. **13** R1 (2005).

Summary



- Electrical conductivities accurate to within a factor of two are needed for many high energy density physics applications --- older models are grossly inadequate in the Warm Dense Matter regime
- Quantum Molecular Dynamics with Density Functional Theory and the Kubo-Greenwood formula have given us an unprecedented level of accuracy for Warm Dense Matter
- Wide range tables tuned to the QMD results allow accurate prediction of magnetically launched flyers and exploding wires starting from the cold solid – manifestly consistent conductivities, equations of state, and opacities
- We've used these methods to obtain new insights into the Equations of State of deuterium, aluminum, tungsten, stainless steel; many more materials are under active study (Cu, Be, Diamond, Au)